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Improving performance of a gas stripping-based recovery system to remove butanol from *Clostridium beijerinckii* fermentation

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Abstract The effect of factors such as gas recycle rate, bubble size, presence of acetone, and ethanol in the solution/broth were investigated in order to remove butanol from model solution or fermentation broth (also called acetone butanol ethanol or ABE or solvents). Butanol (8 g L^{-1}, model solution, Fig. 2) stripping rate was found to be proportional to the gas recycle rate. In the bubble size range attempted (< 0.5 and 0.5–5.0 mm), the bubble size did not have any effect on butanol removal rate (Fig. 3, model solution). In *Clostridium beijerinckii* fermentation, ABE productivity was reduced from 0.47 g L^{-1} h^{-1} to 0.25 g L^{-1} h^{-1} when smaller (< 0.5 mm) bubble size was used to remove ABE (Fig. 4, results reported as butanol/ABE concentration). The productivity was reduced as a result of addition of an excessive amount of antifoam used to inhibit the production of foam caused by the smaller bubbles. This suggested that the fermentation was negatively affected by antifoam.

Keywords Butanol fermentation · Gas bubble size · Selectivity · Gas recycle rate · Stripping rate

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List of symbols

A	Area of the bubble (cm^2)
a	Interfacial area (cm^2)
b	Powers function constants (no units)
c_{10}	Bulk liquid concentration of butanol (mol cm^{-3})
C_s	Solvent concentration in the aqueous phase (mg cm^{-3} or g L^{-1} or kg m^{-3})
C_{s0}	Zero time solvent concentration in the aqueous phase (mg cm^{-3} or g L^{-1} or kg m^{-3})
D	Diffusion coefficient (cm^2 s^{-1})
H	Henry's law constant (atm cm^3 mol^{-1})
H_c	Dimensionless Henry's law constant (no units)
k_g	Gas film mass transfer coefficient for the solvent (cm s^{-1})
k_p	Gas film mass transfer coefficient (based on partial pressure (mol cm^{-2} s^{-1} atm^{-1})
k_l	Liquid film mass transfer coefficient for the solvent (cm s^{-1})
K_p	Overall gas side mass transfer coefficient (mol cm^{-2} s^{-1} atm^{-1})
K_sa	Gas stripping rate constant for solvent in the aqueous phase (s^{-1} or h^{-1})
L	Liquid film thickness (cm, usually 0.01 cm)
m	Power function constant (no units)
N_l	Flux of butanol (mol cm^{-2} s^{-1})
p_{10}	Partial pressure of butanol in the bulk gas bubble (atm)
p_l^*	Hypothetical partial pressure of butanol in equilibrium with the bulk liquid concentration (atm)
Q	Gas flowrate (cm^3 s^{-1})
r	Radius of the bubble (cm)
R	Universal gas constant (82 cm^3 atm mol^{-1} K^{-1})
R_p	Rate of production of solvent (mg cm^{-3} s^{-1} or g L^{-1} h^{-1} or kg m^{-3} h^{-1})
R_s	Rate of solvent stripping from the aqueous phase into the gas phase (mg cm^{-3} s^{-1} or g L^{-1} h^{-1} or kg m^{-3} h^{-1})
t	Time (s or h)

T Absolute temperature (° K)
V Volume of liquid in the reactor (cm^3)

Introduction

The acetone butanol ethanol (ABE or solvents) fermentation process is of interest for production of fuels and chemicals from renewable resources. Butanol is a chemical, which has excellent fuel characteristics. It has higher octane value than ethanol, more miscible with gasoline and diesel, and has lower vapor pressure. Butanol has research and motor octane numbers of 113 and 94 compared to 111 and 92 for ethanol [1]. In addition, butanol, unlike ethanol, separates naturally from water, making it easier to store under humid conditions. It is currently used as a feedstock chemical in the plastic industry and as a food grade extractant in the food and flavor industry.

In the early 1900s, acetone–butanol was the second largest fermentation process, behind only to ethanol. Butanol derived from cheaper petrochemical-based processes started taking over in the 1950s. This resulted in virtual elimination of this fermentation. Environmental concerns and the need to lessen the reliance on diminishing petroleum supplies have renewed interest in obtaining butanol from renewable resources. Butanol has an established market, which continues to grow; with demand around 1.134 billion kg $year^{-1}$ [2]. Unfortunately, economical production of butanol via fermentation is hampered by end-product inhibition, uneconomical product recovery and the use of dilute glucose or starch solutions, thereby resulting in large process stream volumes [3]. Usually, maximum total ABE concentration of 20 g L^{-1} when using *Clostridium acetobutylicum* or *C. beijerinckii* is achieved [4]. The low ABE concentration negatively influences the economics of fermentation-derived butanol relative to petrochemical-derived butanol.

Studies with *C. beijerinckii* BA101 suggest that the developed strain is stable and can be used in a commercial fermentation process for producing butanol from glucose and cornstarch [5, 6]. However, like other butanol-producing microorganisms, butanol is toxic to *C. beijerinckii* BA101. This makes it difficult for *C. beijerinckii* BA101 to accumulate high concentrations. Therefore, to solve this problem, in situ/online butanol removal currently appears to be the most viable path to follow. A variety of alternative methods including membrane-based systems, such as pervaporation [7], perstraction [8], reverse osmosis [9], adsorption [10], liquid–liquid extraction [11–13] and gas stripping [14, 15] were examined. The application of gas stripping results in the use of a concentrated sugar solution in the fermentor [16], a reduction in butanol inhibition and high sugar utilization [17], thereby reducing volumes of the process streams. In such systems, up to 100% utilization of the sugar available in the feed was demonstrated [14].

In recent years, the principles and the adaptability of these simultaneous fermentation and recovery techniques to the butanol fermentation were investigated in the authors' laboratory at the University of Illinois (Urbana, IL, USA). Gas stripping and pervaporation appear to be attractive of the in situ AB fermentation and recovery techniques, but in terms of cost effective industrial application, gas stripping appears to be the most promising. Gas stripping is a technique, which allows for selective removal of volatiles from the fermentation medium and uses no membranes or expensive chemicals. Gas can be sparged into the bioreactor through a sparger, which creates bubbles. When bubbles are formed or broken in bioreactors, the surrounding liquid vibrates resulting in removing volatiles from the reaction mixture. The volatiles can be condensed and separated from the condenser. Bubble size affects mass transfer and mixing hydrodynamics significantly in a gas–liquid agitated vessel [18]. In bioreactors, small gas bubble size maximizes mass transfer, while large gas bubbles maximize recirculation and mixing in the bioreactor.

During ABE fermentation, microorganism growth and product formation in the bioreactor can be limited if the rate of product (butanol) removal from the bioreactor is not optimized. Achieving optimal butanol transfer rate from rising bubbles into the bioreactor headspace and subsequent condensation and removal is of importance to the ABE fermentation. The main objective of our paper was to investigate the influence of gas recycle rate, bubble size, and presence of acetone, and ethanol on the butanol stripping, and selectivity in fermentation using *C. beijerinckii* BA101. In our previous publications [14, 19], effect of gas recycle rate and bubble size was not investigated. As an interest in commercialization of this technology (removal of butanol by gas stripping), it became necessary to study the effect of rate of gas recycle and bubble size on butanol (and ABE) removal from the fermentation broth. Recycle of large amounts of unsaturated gas in large reactors (industrial scale) was not considered to be economical for this fermentation. These studies will be beneficial in commercialization of butanol production by fermentation and recovery by gas stripping and will have a positive impact on the economics of butanol recovery. For these important reasons, these studies are considered novel.

Materials and methods

Microorganism and fermentation conditions

Clostridium beijerinckii BA101 was generated using *N*-methyl-N-nitro-N-nitrosoguanidine (NTG) together with selective enrichment on the nonmetabolizable glucose analog 2-deoxyglucose [20]. Laboratory stocks of

C. beijerinckii BA101 were maintained as spore suspensions in sterile double distilled water at 4°C. Spores (0.2 mL) were heat shocked in cooked meat medium (CCM) (Difco Laboratories, Detroit, MI, USA) containing 30 g L^{-1} glucose at 80°C for 10 min. On incubation at 35°C, The culture was found to be growing actively within 16–18 h. This was followed by transferring 8 cm^3 of the culture to 92 cm^3 of Tryptone–glucose–yeast extract (TGY) medium (in 120 cm^3 screw capped bottle). Cells were grown anaerobically for 4–6 h at 36°C before they were transferred into a 2-L bioreactor containing 60 g glucose L^{-1}; 1 g yeast extract L^{-1} and filter-sterilized P2 stock solutions (g L^{-1}) [(buffer: KH_2PO_4,50; K_2HPO_4,50; Ammonium acetate, 220), (vitamin: Para-amino-benzoic acid, 0.1; Thiamin, 0.1; Biotin, 0.001), (mineral: $MgSO_4.7H_2O$, 20; $MnSO_4.H_2O$, 1; $FeSO_4.7H_2O$, 1; NaCl, 1)] [21].

Experimental apparatus and procedures

The experimental apparatus shown in Fig. 1a consists of a bioreactor with bubble delivery device, a condenser, and a variable speed pump. Gas stripping experiments in which an 8 g L^{-1} butanol solution or ABE model solution containing 5, 10, and 1 g L^{-1} ABE, respectively were carried out using a sparger or impeller for gas bubble delivery. One liter of liquid volume (butanol model solution, ABE model solution or fermentation broth) in a 2 L bioreactor was used in all cases during gas stripping and recovery. The temperature in the bioreactor was maintained at 35–36°C under atmospheric pressure. Gas stripping was initiated by passing N_2 via the impeller or sparger to create gas bubbles in the glass bioreactor. These two systems were used to increase the rate of mass transfer by manipulating interfacial area (a) and gas-flow rate in the bioreactor. The N_2 was recycled through the system (43 or 80 cm^3 s^{-1}) using a twin-head peristaltic pump. The cooling machine (GeneLine) was obtained from Beckman Instruments (Palo Alto, CA, USA). The ABE vapors were cooled in a condenser (62×600 mm and cooling coil surface area 1,292 cm^2) to 3°C, using ethylene glycol (50% v/v) circulated at a flow rate of 600 cm^3 min^{-1} through the condenser. Compensation for water loss was not made during the course of the model stripping experiments. Antifoam 204 (Sigma chemicals, St. Louis, MO, USA) was used as an antifoam agent and was added manually. Samples were withdrawn at intervals for ABE analysis.

Estimation of flow rates and gas bubble sizes

Gas-flow rate was measured using the timed water displacement method. Nitrogen gas was pumped into a closed airtight 10-L vessel containing distilled water. Water flowed out of the vessel, (via a tube that was situated below the water level) due to the gas pumped in,

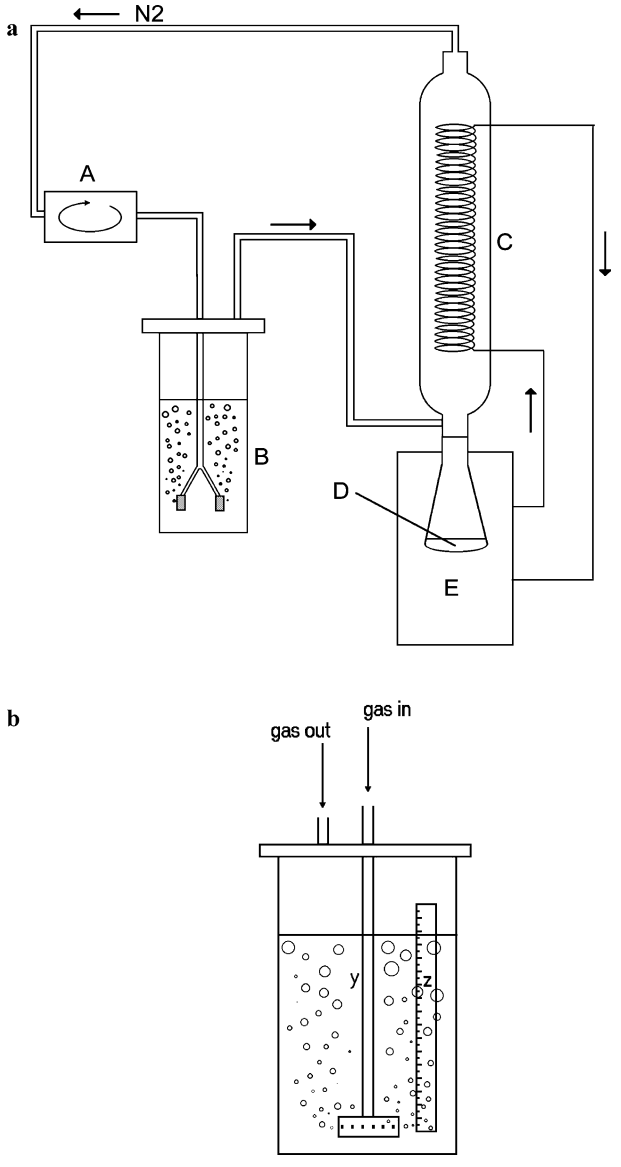

Fig. 1 **a** A schematic diagram showing in situ butanol recovery by gas stripping (gas sparger system). *A* gas recycle pump with variable speed; *B* bioreactor with gas sparger; *C* condenser; *D* condensed ABE vapors; *E* Cooling apparatus with coolant. **b** Bioreactor with impeller. *Y*impeller, *Z* ruler

and was collected for a timed period. Flow rate was calculated as volume of displaced water over time. Both the gas inlet and water outlet were at atmospheric pressure and large diameter tubes were used to avoid pressure buildup.

For the estimation of gas bubble sizes, gas was bubbled through the system using either a sparger or an impeller set at flow rates of 43 or 80 cm^3 s^{-1} (Fig. 1a, b). Pictures of the bioreactor were taken using a digital camera for bubble size measurement. The bubble size population was estimated visually as a range using a ruler inserted inside the bioreactor for scale. The bubble sizes determined were assumed constant for the bubble

delivery apparatus (sparger or impeller) used at the flow rate measured throughout the study.

Batch fermentation and gas stripping

A bioreactor containing 60 g glucose L^{-1} and 1 g yeast extract L^{-1} (1.0-L reaction volume) was sterilized at 121°C for 15 min. On cooling to 35°C under an oxygen-free nitrogen atmosphere, filter-sterilized P2 stock solutions were added [21]. The bioreactor was inoculated with 5% (v/v; 5 cm^3 culture to 95 cm^3 medium) highly motile cells of *C. beijerinckii* BA101. Oxygen-free nitrogen gas was swept over the headspace of the bioreactor until the culture produced its own gases (CO_2 and H_2). Batch fermentations were allowed to proceed for 20 h when the ABE concentrations approached 2.0–2.5 g L^{-1}, after which gas stripping (Fig. 1a) was initiated at gas-flow rate of 80 cm^3 s^{-1}. Samples were aseptically withdrawn at intervals for analysis.

Analytical procedures

ABE and acids (acetic and butyric) were measured using a 6890 Hewlett-Packard gas chromatograph (Hewlett Packard, Avondale, PA, USA) equipped with a flame ionization detector (FID) and 1,829×2 mm glass column (10% CW-20 M, 0.01% H_3PO_4, support 80/100 Chromosorb WAW). Productivity was calculated as total ABE concentration (g L^{-1}) divided by the fermentation time (h). Although, for mathematical equations, rate of production or removal of ABE was calculated as mg cm^{-3} s^{-1}, for convenience it was presented as g L^{-1} h^{-1} (Fig. 2). ABE or butanol concentration was plotted as g L^{-1} (Fig. 4) rather than mg cm^{-3}. Similarly bubble size was presented in mm (Fig. 3) rather than in cm. Also K_sa value was presented in h^{-1} (Table 1 and text) rather than s^{-1}. Selectivity is calculated as $\alpha = [y/(1-y)]/[x/(1-x)]$, where x and y are weight fractions of acetone, butanol and ethanol in fermentation broth and condensate, respectively. Stripping rate was determined as the derivative of time–butanol concentration data exponential best fit curve following the equations: $R_s = -dC_s/dt = K_s a C_s C_s = C_{so} e^{-K_s at} \cdot K_s a$ (stripping rate constant) was determined as the slope of concentration-stripping rate linear best-fit curve.

Glucose concentration was determined using a hexokinase and glucose-6-phosphate dehydrogenase (Sigma chemicals) coupled enzymatic assay as previously described [22].

Results and discussion

Effect of gas-stripping rate constant, bubble size, and gas-flow rate on stripping

Gas stripping of butanol and other organic solvents from an aqueous solution can be modeled as a first-order process according to the following equation reported by Truong and Blackburn [23].

$$R_s = \frac{-dC_s}{dt} = K_s a C_s \quad (1)$$

By Eq. 1, the gas stripping rate increases proportionally, both for changes in concentration and K_sa. For the system under study, in which butanol, the product being stripped, is both a desired product and an inhibitory compound to the microorganism producing it. The relationship between stripping rate and butanol concentration is dually beneficial. As *C. beijerinckii*

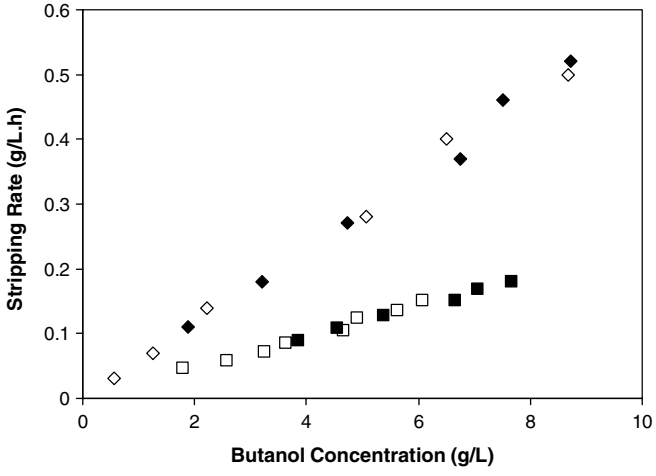

Fig. 2 Stripping rate versus concentration in a model solution containing 8 g butanol L^{-1}. Two gas bubble delivery systems, impeller and sparger were used at 43 and 80 cm^3 s^{-1} gas recycle rate. Symbols: *filled diamond*, sparger 80 cm^3 s^{-1}; *open diamond*, impeller 80 cm^3 s^{-1}; *filled square*, sparger 43 cm^3 s^{-1}; *open square* impeller 43 cm^3 s^{-1}

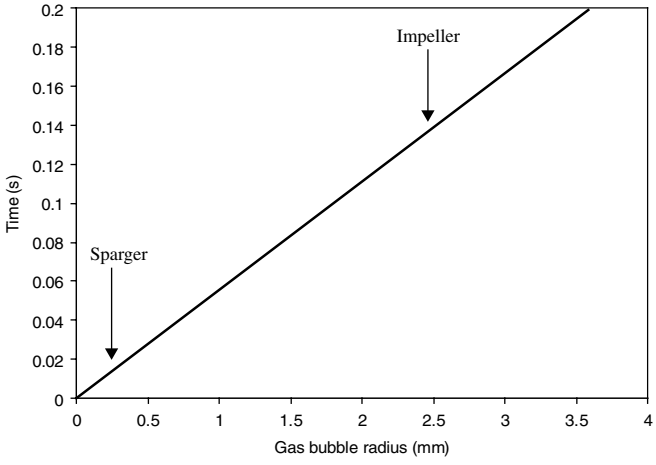

Fig. 3 Time to reach 95% saturation with butanol in spherical gas bubbles produced by sparger and impeller based gas bubble delivery systems. *Arrow* shows the time when the gas bubble reached 95% saturation with butanol

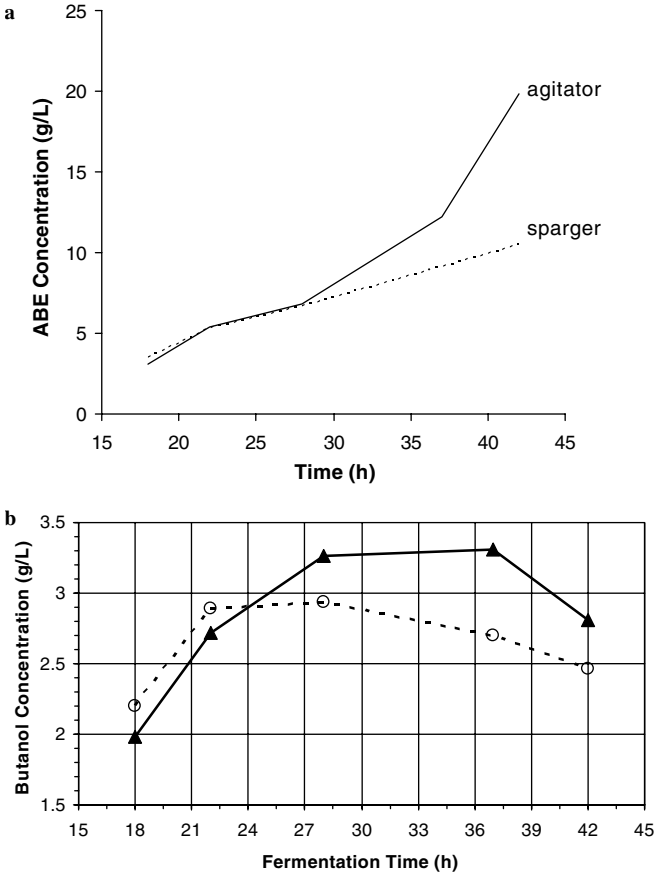

Fig. 4 **a** Effect of impeller and sparger based gas bubble delivery systems on total ABE production by *C. beijerinckii* BA101, **b** Butanol concentration in bioreactor during gas stripping using sparger and impeller based gas bubble delivery systems. Symbols: *filled triangle,* impeller; *open circle,* sparger

BA101 produces butanol, the rate at which it is removed from the fermentation broth likewise increases (Eq. 1). For a system in which butanol is both being produced and stripped, such as in a fermentation with stripping, change in butanol concentration is given by the following equation:

Table 1 Various parameters during butanol recovery by gas stripping

Treatments	Device	Gas recycle rate ($cm^3\ s^{-1}$)	K_sa (butanol) (h^{-1})	Selectivity (butanol) (no units)
Model butanol Solution	Impeller	80	0.059	6.3
	Sparger	80	0.059	6.3
	Impeller	43	0.024	6.2
	Sparger	43	0.023	5.6
Model ABE solution with cells	Impeller	80	0.058	6.3
	Sparger	80	0.027	6.1
ABE fermentation broth	Impeller	80	ND	9.0
	Sparger	80	ND	8.7

ND not detected

$$\frac{-dC_s}{dt} = R_s - R_p = K_s a C_s - R_p \quad (2)$$

At steady state (d C_s/d $t = 0$), the following relationship is obtained:

$$R_s = R_p = K_s a C_s \quad (3)$$

This equation indicates that if K_sa can be increased, then *C. beijerinckii* BA101 will be subjected to a lower concentration of inhibitory solvent for any given rate of solvent production. It is our goal in this study to manipulate the parameter K_sa through physical adjustments to the gas stripping process to achieve this affect.

For a two-film mass transfer model for volatilization processes, the gas-stripping rate constant can be modeled as [23]:

$$K_s a = \frac{a}{V}\left[\frac{1}{k_1} + \frac{RT}{H_c k_g}\right]^{-1} \quad (4)$$

In the current investigation, we attempted to increase the rate of mass transfer by manipulating the parameter a. The gas-stripping rate constant, K_sa, was determined when using two types of bubble delivery devices that produce different bubble size populations. By decreasing the bubble size for a set gas flowrate, the total interfacial surface area is increased, which gives a corresponding increase in K_sa according to Eq. 4.

Troung and Blackburn [23] developed a correlation in which gas flowrate is related to K_sa for organic compounds in water.

$$K_s a \frac{V}{Q} = b(H_c)^m \quad (5)$$

By manipulating gas flowrate, Q, the value of K_sa is likewise changed. We used two flow rates in order to examine if a higher stripping rate could be achieved by increasing gas flowrate. The important relationships obtained from Eqs. 1, 4, and 5 are:

$$R_s \propto K_s a \quad (6)$$

$$K_s a \propto a \quad (7)$$

$$K_s a \propto Q \quad (8)$$

Experiments were performed in order to verify these systems for the biological process under investigation. Figure 2 shows experimental data in which a flowrate, Q, of 80 or 43 $cm^3\ s^{-1}$ was used and either an impeller or sparger was used to deliver gas bubbles. The interfacial area created by sparger corresponds to an unquantified high a, and the impeller a low a. In Fig. 2, the slope of the regressed data points for each dataset is the experimentally obtained K_sa for that data set. For both datasets that were run at a flowrate of 80 $cm^3\ s^{-1}$, a K_sa of 0.059 h^{-1} was obtained. For the sparger and impeller run at a flowrate of 43 $cm^3\ s^{-1}$, K_sa's of 0.023 and 0.024 h^{-1} were obtained respectively. These results

indicate that the relationship given in Eq. 7 holds. For a 1.86-fold increase in gas flowrate, a 2.51-fold increase in gas-stripping rate constant ($K_s a$) is obtained at any solvent concentration (Eq. 6). A one to one relationship between gas-flow rate increase and $K_s a$ increase was expected based on Eq. 6. The discrepancy may be attributed to added turbulence at the higher gas-flow rate. Also, it is likely that the pump contributed some heat at the higher flow rate that increased the stripping rate constant.

The relationship given in Eq. 7, however, did not hold in the experiments performed. The difference in bubble size appears to have no effect on $K_s a$. The number and size (0.5–5–mm diameter) of gas bubbles from the impeller seem to be sufficient for quick butanol saturation (with gas bubbles) during their contact time in the bioreactor. Therefore, reducing the size of the bubbles would offer no capacity for increasing the rate of mass transfer. This hypothesis was tested mathematically by calculating the time, a model spherical bubble of gas would take to reach 95% saturation with butanol when in contact with an aqueous solution containing a fixed concentration of butanol. A fixed butanol concentration is used because it is assumed that the butanol concentration in aqueous solution does not change noticeably during the time it takes for one bubble to pass through the bioreactor (< 1 s). A schematic diagram of a gas bubble in liquid butanol solution is shown below.

The overall mass balance can be expressed as

$$\frac{V}{RT}\cdot\frac{\mathrm{d}p_{10}}{\mathrm{d}t} = N_1 A \tag{9}$$

with

$$V = \frac{4}{3}\pi r^3 \tag{9a}$$

and

$$A = 4\pi r^2. \tag{9b}$$

These equations can be combined with the following mass transfer equation [24]

$$N_1 = (p_1^* - p_{10})K_\mathrm{p} \tag{10}$$

Combining Eqs. 9 and 10 yields Eq. 11.

$$\frac{\mathrm{d}p_{10}}{(p_1^* - p_{10})} = \frac{3RTK_\mathrm{p}}{r}\mathrm{d}t \tag{11}$$

Integration of Eq. 11 with the following boundary conditions:

$$\begin{aligned} &p_{10} = 0 \text{ at } t = 0,\ p_{10} = 0.95p_1^* \text{ at } t = \mathrm{t} \\ &\text{gives the folowing relationship } r = 1.75t \end{aligned} \tag{12}$$

The Appendix details how Eq. 12 was developed from Eq. 11.

Equation 12 indicates that the larger bubbles (radius = 2.5 mm) should become 95% saturated in only 0.14 s as shown in Fig. 3. Therefore, the gas bubbles formed in the bioreactor have sufficient time to become saturated with butanol and using smaller bubbles would not increase mass transfer.

Experiments were also performed (data not shown) using model solutions containing acetone, butanol and ethanol, which confirmed that the presence of acetone and ethanol did not affect the stripping rate of butanol, neither in terms of $K_s a$ nor in terms of selectivity. In experiments performed, in which inactive *C. beijerinckii* BA101 cells were added to a model solution containing butanol, similar $K_s a$s and selectivities were obtained as with a model solution containing only butanol when the impeller was used (Table 1). However, the bioreactor foamed continuously when the sparger was used. Much lower $K_s a$ (0.027 h^{-1}) was obtained due to the effect of antifoam on the stripping rate of butanol. The addition of antifoam to bioreactors is known to affect hydrodynamics, bubble behavior and interactions, and tend to reduce the specific interfacial area available for mass transfer [25].

Fermentation and gas stripping

From results obtained using model solutions, it appeared that the impeller and sparger would equally be effective in removing butanol from the fermentation broth of ABE fermentation. When experiments were performed to test this hypothesis, a practical problem arose with the use of the sparger. The tiny bubbles produced by the sparger created excessive amounts of foam in the bioreactor, necessitating the addition of more antifoam than was used in the bioreactor that used an impeller. This resulted in an overall lower production of ABE during the fermentation. This is attributed to the toxic effect of antifoam on the *C. beijerinckii* BA101 culture. Nearly twice the amount of ABE was produced in the bioreactor using the impeller (Fig. 4a). High butanol concentration in the fermentation medium was also linked to clostridial cells degeneration and low butanol productivity. It should be noted that butanol productivities for *C. beijerinckii* BA101 was progressively reduced by concentrations of butanol between 7.5 g L^{-1} and 17.5 g L^{-1} [26]. In another investigation, butanol concentrations between 7 and 16 g L^{-1} in the bioreactor were shown to induce progressive levels of cell autolysis and degeneration of *C. acetobutylicum* P262 [27]. However, both impeller and sparger systems kept the butanol concentration in the bioreactor below 3.5 g L^{-1} during fermentation and gas stripping recovery process (Fig. 4b).

Conclusions

Of the several factors tested, the rate of gas recycle and addition of excessive amounts of antifoam were found to affect the solvent/ABE recovery system. Gas recycle

rates of 80 $cm^3\ s^{-1}$ and a K_sa of 0.058 h^{-1} are sufficient for keeping the butanol concentration below toxic levels in a 2-L bioreactor (1-L reaction volume) during the course of the ABE fermentation. It was demonstrated that bubble sizes < 0.5 and 0.5–5.0 mm had no effect on the stripping rate of butanol under the conditions tested. When the sparger was employed in an actual batch fermentation employing *C. beijerinckii*, smaller bubbles (size, <0.5 mm) led to large amounts of foam in the reactor, which required the addition of high levels of antifoam thus affecting ABE production negatively. The ABE productivities of the bioreactor using an impeller (larger size bubble delivery system) or sparger (smaller size bubble delivery system) based gas delivery systems were 0.47 and 0.25 g $L^{-1}\ h^{-1}$, respectively. The presence of acetone, and ethanol (using a model solution) had no affect on butanol removal rate. It is recommended that a gas bubble size in the range of 0.5–5 mm in diameter (produced by the impeller) be used for gas stripping to provide good mass transfer and avoid problems associated with excessive foaming.

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Appendix

Integration of Eq. 11 with the stated boundary conditions yields:

$$r = RTK_p t$$

p_1^* is considered a constant for the integration because the bulk liquid butanol concentration, c_{10}, is assumed to be constant and

$$p_1^* = Hc_{10}$$

$$K_p = \frac{1}{(1/k_p) + (H/k_1)} \quad \text{cussler [24]}$$

$$k_p \approx D/(LRT) \quad \text{cussler [24]}$$

$$k_1 \approx D/L$$

where $L = 0.01$ cm in the above two equations) cussler [24]

$$D \propto T^{3/2} \quad \text{cussler [24]}$$

For butanol in air at 299.1 K, $D = 0.087\ cm^2\ s^{-1}$. For butanol in water at 298 K, $D = 7.7\ 10^{-6}\ cm^2\ s^{-1}$. Adjusting for temperature (310 K for water and 290 K for air) yields $D = 0.083\ cm^2\ s^{-1}$ and $8.2\times10^{-6}\ cm^2\ s^{-1}$. Therefore, $k_p$and k_l are 3.49×10^{-4} mol $cm^{-2}\ s^{-1}\ atm^{-1}$ and $8.2\times10^{-4}\ cm\ s^{-1}$ respectively. Using $H = 8.81$ atm $cm^3\ mol^{-1}$ [28] gives $K_p = 7.35\times10^{-5}$ mol $cm^{-2}\ s^{-1}\ atm^{-1}$. Substitution of K_p, R (82 cm^3 atm $mol^{-1}\ K^{-1}$), and T (290 K) yields Eq. 12.

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